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Description

Method for producing structured adhesive materials and the use of the same

The invention relates to a method of producing structured pressure-sensitive adhesives (PSAs), especially acrylate pressure-sensitive adhesives (acrylate PSAs), to their use for producing pressure-sensitive adhesive tapes (PSA tapes), and to pressure-sensitive adhesive tapes which comprise a pressure-sensitive adhesive (PSA) of this kind.

For acrylate PSAs there exist a multiplicity of applications. For instance, these PSA tapes find application in automobiles, boats, aircraft, in house building, in the electrical sector, and for joining mechanical parts.

Depending on application, these acrylate PSAs possess very different properties. For permanent bonds, high bond strengths are frequently required, and the PSA ought also to possess a high internal strength (cohesion). Other bonds are performed only on a temporary basis, and so for this purpose, generally speaking, lower bond strengths are needed. A particularly interesting field is that of PSAs having anisotropic properties. Here, PSAs develop significantly higher or lower bond strengths in one direction. This can be very useful, since very high bond strengths can be realized in one load direction, and the bond is therefore very stable, but in another direction the bond, in turn, can easily be parted.

Techniques of structuring have already been known for a long time from lithography. Patents US 5,910,392, US 5,861,231; US 4,968,581; US 4,883,740; US 4,810,613, and US 4,491,628, for example, describe such techniques. However, these techniques are difficult to incorporate into an operation for producing PSA tapes.

DE 100 08 844.9 and DE 100 08 840.6 describe operations for structuring acrylate PSAs. With these, however, it is not possible to obtain anisotropic properties.

There is therefore a need for a method of producing structured acrylate PSAs which exhibit anisotropic adhesion properties.

The object on which the invention is based is therefore to specify a method of producing structured PSAs which exhibit anisotropic adhesion properties. The intention, furthermore, is to specify uses of such PSA, and also PSA tapes which comprise such PSA.

This object is achieved through the features of claims 1, 10, 11, 12, and 13. Advantageous embodiments of the inventions arise from the features of claims 2 to 9.

In accordance with the invention a method is provided of producing structured pressure-sensitive adhesives, in which the pressure-sensitive adhesive is coated from the melt through a die, is structured by the die, and subsequently is crosslinked with actinic radiation.

The pressure-sensitive adhesive is preferably an acrylate PSA.

Fig. 1 shows different cross sections of dies a to l which are used advantageously for the method of the invention.

The method of the invention advantageously comprises (a) coating a pressure-sensitive adhesive, preferably an acrylate pressure-sensitive adhesive, from the melt through a structured die onto a backing material or water, and (b) freezing the resultant structured pressure-sensitive adhesive on the backing material or the water by means of crosslinking with actinic radiation.

In accordance with the invention this method is carried out preferably in a unit which comprises a die which at the die exit bears a structural element which is to be transmitted to the pressure-sensitive adhesive, and a crosslinking unit, which is composed preferably of UV lamps and/or electron accelerators.

In one preferred embodiment the dies for coating from the melt possess the outlet structures depicted in fig. 1. As a result of this shaping in the die or at the die outlet, the structure is generated in the pressure-sensitive adhesive. The structures generated are formed in correspondence with the mirror image of excavations located in the die.

Shaping takes place in the longitudinal direction; that is, parallel to the flow direction. It is also possible for the structures depicted at the top to be generated. In this way it is possible, accordingly, to generate circular, oval, angular, rectangular, square, triangular, jagged, sawtoothlike or edged structures. The PSA may be structured on the top face, structured on the bottom face, and structured both on the top face and on the bottom face.

The structures generated may also differ from the patterns depicted above; that is, they may differ, for example, in shape and in size. As a result of the coating operation, however, there is always an orientation in the longitudinal direction.

For coating it is preferred to use acrylate PSAs. The polymers preferably possess the following composition:

acrylic esters and/or methacrylic esters or the free acids thereof, with the following formula

$$CH_2 = CH(R_1)(COOR_2),$$

where R_1 = H or CH_3 and R_2 is an alkyl chain having 1 - 30 carbon atoms or H, with a fraction of at least 50% by weight in the composition.

For the polymerization the monomers are chosen such that the resulting polymers can be used, at room temperature or higher temperatures, as PSAs, particularly such that the resulting polymers possess pressure-sensitive adhesion properties in accordance with the "Handbook of Pressure Sensitive Adhesive Technology" by Donatas Satas (van Nostrand, New York 1989).

In order to achieve a preferred polymer glass transition temperature T_g of $\leq 10°C$ it is very preferred, in accordance with the comments made above, to select the monomers in such a way, and to choose the quantitative composition of the monomer mixture advantageously in such a way, as to result in the desired T_g for the polymer in accordance with the ***Fox*** equation (E1) (cf. T.G. Fox, Bull. Am. Phys. Soc. 1 (1956) 123).

$$\frac{1}{T_g} = \sum_n \frac{w_n}{T_{g,n}} \qquad \text{(E1)}$$

In this equation, n represents the serial number of the monomers used, w_n the mass fraction of the respective monomer n (% by weight), and $T_{g,n}$ the respective glass

transition temperature of the homopolymer of each of the monomers n, in K.

In one very preferred embodiment, acrylic or methacrylic monomers are used which comprise acrylic and methacrylic esters having alkyl groups composed of 4 to 14 carbon atoms, preferably 4 to 9 carbon atoms. Specific examples, without wishing to be restricted by this enumeration, are methyl acrylate, methyl methacrylate, ethyl acrylate, n-butyl acrylate, n-butyl methacrylate, n-pentyl acrylate, n-hexyl acrylate, n-heptyl acrylate, n-octyl acrylate, n-octyl methacrylate, n-nonyl acrylate, lauryl acrylate, stearyl acrylate, behenyl acrylate; and the branched isomers thereof, such as isobutyl acrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, isooctyl acrylate, and isooctyl methacrylate, for example.

Further classes of compound to be used with preference are monofunctional acrylates and/or methacrylates of bridged cycloalkyl alcohols composed of at least 6 carbon atoms. The cycloalkyl alcohols may also be substituted, by C_{1-6} alkyl, halogen or cyano, for example. Specific examples are cyclohexyl methacrylates, isobornyl acrylate, isobornyl methacrylates, and 3,5-dimethyladamantyl acrylate.

In one embodiment monomers are used which carry at least one polar group such as carboxyl, sulfonic and phosphonic acid, hydroxyl, lactam and lactone, N-substituted amide, N-substituted amine, carbamate, epoxy, thiol, ether, alkoxy, cyano or the like.

Moderate basic monomers are, for example, N,N-dialkyl-substituted amides, such as, for example, N,N-dimethylacrylamide, N,N-dimethylmethylmethacrylamide, N-tert-butylacrylamide, N-vinylpyrrolidone, N-vinyllactam, dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, diethylaminoethyl methacrylate, diethylaminoethyl acrylate, N-methylolmethacrylamide, N-(buthoxymethyl)methacrylamide, N-methylolacrylamide, N-(ethoxymethyl)acrylamide, and N-isopropylacrylamide, this enumeration not being exhaustive.

Further preferred examples are hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, allyl alcohol, maleic anhydride, itaconic anhydride, itaconic acid, glyceridyl methacrylate, phenoxyethyl acrylate, phenoxyethyl methacrylate, 2-butoxyethyl methacrylate, 2-butoxyethyl acrylate, cyanoethyl methacrylate, cyanoethyl acrylate, glyceryl methacrylate, 6-hydroxyhexyl methacrylate, vinylacetic acid, tetrahydrofurfuryl acrylate, β-acryloyloxypropionic acid,

trichloroacrylic acid, fumaric acid, crotonic acid, aconitic acid, and dimethylacrylic acid, this enumeration not being exhaustive.

Moreover, in one further embodiment, use is made of photoinitiators having a copolymerizable double bond. Suitable photoinitiators are Norrish type I and II. Examples include benzoin acrylate and an acrylated benzophenone from UCB (Ebecryl P 36®). This enumeration is not complete. In principle it is possible to copolymerize any photoinitiators which are known to the skilled worker and which are able to crosslink the polymer by way of a free-radical mechanism under UV irradiation.

In one further very preferred embodiment the monomers used include vinyl esters, vinyl ethers, vinyl halides, vinylidene halides, and vinyl compounds having aromatic rings and heterocycles in α position. Here again, mention may be made, nonexclusively, of some examples: vinyl acetate, vinylformamide, vinylpyridine, ethyl vinyl ether, vinyl chloride, vinylidene chloride, and acrylonitrile.

In another preferred embodiment the comonomers described are admixed with monomers which possess a high static glass transition temperature. Suitable components include aromatic vinyl compounds, an example being styrene, in which the aromatic nuclei consist preferably of C_4 to C_{18} and may also include heteroatoms. Particularly preferred examples are 4-vinylpyridine, N-vinylphthalimide, methylstyrene, 3,4-dimethoxystyrene, 4-vinylbenzoic acid, benzyl acrylate, benzyl methacrylate, phenyl acrylate, phenyl methacrylate, t-butylphenyl acrylate, t-butylphenyl methacrylate, 4-biphenylyl acrylate and methacrylate, 2-naphthyl acrylate and methacrylate, and mixtures of these monomers, this enumeration not being exhaustive.

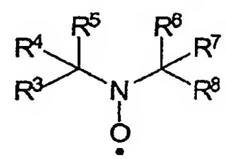
For the preparation of the poly(meth)acrylate PSAs it is advantageous to carry out conventional free-radical polymerizations. For the polymerizations which proceed free-radically it is preferred to employ initiator systems which also contain further free-radical initiators for the polymerization, especially thermally decomposing, free-radical-forming azo or peroxo initiators. In principle, however, all customary initiators for acrylates which are familiar to the skilled worker are suitable for this purpose. The production of C-centered radicals is described in Houben Weyl, Methoden der Organischen Chemie, Vol. E 19a, pp. 60 – 147. These methods are employed, preferentially, in analogy.

Examples of free-radical sources are peroxides, hydroperoxides, and azo compounds.

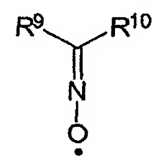
Some nonlimiting examples of typical free-radical initiators that may be mentioned here include potassium peroxodisulfate, dibenzoyl peroxide, cumene hydroperoxide, cyclohexanone peroxide, di-t-butyl peroxide, azodiisobutyronitrile, cyclohexylsulfonyl acetyl peroxide, diisopropyl percarbonate, t-butyl peroctoate, and benzpinacol. In one very preferred embodiment the free-radical initiator used is 1,1'-azobis(cyclohexane-carbonitrile) (Vazo 88™ from DuPont) or azodiisobutyronitrile (AIBN).

For preparing the polyacrylates it is also possible, however, in principle to use any polymerizations which proceed by controlled-growth or living mechanisms, including combinations of different controlled polymerization processes. Mention may be made here by way of example without claim to completeness, and besides anionic polymerization, of ATRP, the nitroxide/TEMPO-controlled polymerization, or, more preferably, the RAFT process.

For free-radical stabilization, in a favorable procedure, use is made of nitroxides of type (Ia) or (Ib):



(Ia)



(Ib)

where R^3, R^4, R^5, R^6, R^7, R^8, R^9, and R^{10} are chosen independently of one another and denote the following compounds or atoms:

i) halides, such as chlorine, bromine or iodine, for example;
ii) linear, branched, cyclic, and heterocyclic hydrocarbons having 1 to 20 carbon atoms, which may be saturated, unsaturated or aromatic;
iii) esters $-COOR^{11}$, alkoxides $-OR^{12}$ and/or phosphonates $-PO(OR^{13})_2$, where R^{11}, R^{12} or R^{13} stand for radicals from group ii).

Compounds of (Ia) or (Ib) may also be attached to polymer chains of any kind.

More strongly preferred are controlled regulators for the polymerization of compounds of the following type:

- 2,2,5,5-tetramethyl-1-pyrrolidinyloxyl (PROXYL), 3-carbamoyl-PROXYL, 2,2-dimethyl-4,5-cyclohexyl-PROXYL, 3-oxo-PROXYL, 3-hydroxylimine-PROXYL, 3-aminomethyl-

PROXYL, 3-methoxy-PROXYL, 3-t-butyl-PROXYL, 3,4-di-t-butyl-PROXYL;

- 2,2,6,6-tetramethyl-1-piperidinyloxy pyrrolidinyloxyl (TEMPO), 4-benzoyloxy-TEMPO, 4-methoxy-TEMPO, 4-chloro-TEMPO, 4-hydroxy-TEMPO, 4-oxo-TEMPO, 4-amino-TEMPO, 2,2,6,6,-tetraethyl-1-piperidinyloxyl, 2,2,6-trimethyl-6-ethyl-1-piperidinyloxyl;
- N-tert-butyl 1-phenyl-2-methylpropyl nitroxide;
- N-tert-butyl 1-(2-naphthyl)-2-methylpropyl nitroxide;
- N-tert-butyl 1-diethylphosphono-2,2-dimethylpropyl nitroxide;
- N-tert-butyl 1-dibenzylphosphono-2,2-dimethylpropyl nitroxide;
- N-(1-phenyl-2-methylpropyl) 1-diethylphosphono-1-methylethyl nitroxide;
- di-t-butyl nitroxide;
- diphenyl nitroxide;
- t-butyl t-amyl nitroxide.

A series of further polymerization methods in accordance with which the PSAs can be prepared by an alternative procedure can be chosen from the prior art:
US 4,581,429 A discloses a controlled-growth free-radical polymerization process which uses as its initiator a compound of the formula R'R"N-O-Y, in which Y is a free-radical species which is able to polymerize unsaturated monomers. In general, however, the reactions have low conversion rates. A particular problem is the polymerization of acrylates, which takes place only with very low yields and molar masses. WO 98/13392 A1 describes open-chain alkoxyamine compounds which have a symmetrical substitution pattern. EP 735 052 A1 discloses a process for preparing thermoplastic elastomers having narrow molar mass distributions. WO 96/24620 A1 describes a polymerization process in which very specific free-radical compounds, such as phosphorus-containing nitroxides based on imidazolidine, for example, are employed. WO 98/44008 A1 discloses specific nitroxyls based on morpholines, piperazinones, and piperazinediones. DE 199 49 352 A1 describes heterocyclic alkoxyamines as regulators in controlled-growth free-radical polymerizations. Corresponding further developments of the alkoxyamines or of the corresponding free nitroxides improve the efficiency for the preparation of polyacrylates (Hawker, paper to the National Meeting of the American Chemical Society, Spring 1997; Husemann, paper to the IUPAC World-Polymer Meeting 1998, Gold Coast).

As a further controlled polymerization method, atom transfer radical polymerization (ATRP) can be used advantageously to synthesize the block copolymers, in which case

use is made preferably as initiator of monofunctional or difunctional secondary or tertiary halides and, for abstracting the halide(s), of complexes of Cu, Ni, Fe, Pd, Pt, Ru, Os, Rh, Co, Ir, Ag or Au (EP 0 824 111 A1; EP 826 698 A1; EP 824 110 A1; EP 841 346 A1; EP 850 957 A1). The various possibilities of ATRP are further described in US 5,945,491 A, US 5,854,364 A and US 5,789,487 A.

The average molecular weights M_n of the PSAs formed in the polymerization are very preferably chosen such that they are situated within a range of 20 000 to 2 000 000 g/mol; specifically for further use as hot-melt PSAs, PSAs are prepared which have average molecular weights M_n of 100 000 to 500 000 g/mol. The average molecular weight is determined by size exclusion chromatography (GPC) or matrix-assisted laser desorption/ionization coupled with mass spectrometry (MALDI-MS).

The polymerization may be conducted without solvent, in the presence of one or more organic solvents, in the presence of water, or in mixtures of organic solvents and water. The aim is to minimize the amount of solvent used. Suitable organic solvents are straight alkanes (e.g., hexane, heptane, octane, isooctane), aromatic hydrocarbons (e.g., benzene, toluene, xylene), esters (e.g., ethyl, propyl, butyl or hexyl acetate), halogenated hydrocarbons (e.g., chlorobenzene), alkanols (e.g., methanol, ethanol, ethylene glycol, ethylene glycol monomethyl ether), and ethers (e.g., diethyl ether, dibutyl ether) or mixtures thereof. A water-miscible or hydrophilic cosolvent may be added to the aqueous polymerization reactions in order to ensure that the reaction mixture is present in the form of a homogeneous phase during monomer conversion. Cosolvents which can be used with advantage for the present invention are chosen from the following group, consisting of aliphatic alcohols, glycols, ethers, glycol ethers, pyrrolidines, N-alkylpyrrolidinones, N-alkylpyrrolidones, polyethylene glycols, polypropylene glycols, amides, carboxylic acids and salts thereof, esters, organic sulfides, sulfoxides, sulfones, alcohol derivatives, hydroxy ether derivatives, amino alcohols, ketones and the like, and also derivatives and mixtures thereof.

The polymerization time - depending on conversion and temperature - is between 4 and 72 hours. The higher the reaction temperature which can be chosen, i.e., the higher the thermal stability of the reaction mixture, the shorter can be the chosen reaction time.

As regards initiation of the polymerization, the introduction of heat is essential for the thermally decomposing initiators. For these initiators the polymerization can be initiated

by heating to from 50 to 160°C, depending on initiator type.

Another advantageous preparation process for the polyacrylate PSAs is that of anionic polymerization. In this case the reaction medium used preferably comprises inert solvents, such as aliphatic and cycloaliphatic hydrocarbons, for example, or else aromatic hydrocarbons.

For UV crosslinking it is preferred to add UV photoinitiators. The photoinitiators may be of the Norrish I or Norrish II type. Certain groups of photoinitiators may be listed, as follows: benzophenone, acetophenone, benzil, benzoin, hydroxyalkylphenone, phenyl cyclohexyl ketone, anthraquinone, trimethylbenzoylphosphine oxide, methylthiophenyl morpholine ketone, aminoketone, azobenzoin, thioxanthone, hexaarylbisimidazole, triazine or fluorenone, it being possible for each of these radicals to be additionally substituted by one or more halogen atoms and/or by one or more alkoxy groups and/or by one or more amino groups or hydroxyl groups. A representative overview is given in "Photoinitiation, Photopolymerization and Photocuring: Fundamentals and Applications", by J.-P. Fouassier, Hanser Publishers, Munich, Vienna, New York 1995". For further details it is possible to consult "Chemistry and Technology of UV and EB Formulation for Coatings, Inks and Paints, Volume 5, A. Carroy, C. Decker, J.P. Dowling, P. Pappas, B. Monroe, ed. by P.K.T. Oldring, publ. by SITA Technology, London, England 1994".

For crosslinking with actinic radiation the PSA is optionally blended with a crosslinker. Preferred substances which crosslink under radiation in accordance with the method are, for example, difunctional or polyfunctional acrylates or difunctional or polyfunctional urethane acrylates or difunctional or polyfunctional methacrylates. Simple examples thereof are 1,6-hexanediol diacrylate, pentaerythritol acrylate, trimethylolpropane triacrylate or 1,2-ethylene glycol diacrylate. It is, however, also possible here to use all further difunctional or polyfunctional compounds, familiar to the skilled worker, which are capable of crosslinking polyacrylates under radiation.

To modify the adhesion properties of the poly(meth)acrylates prepared, as pressure-sensitive adhesives, the polymers are optimized by optional blending with at least one resin. As tackifying resins for addition it is possible without exception to use all existing tackifier resins and those described in the literature. Representatives that may be mentioned include pinene resins, indene resins and rosins, their disproportionated, hydrogenated, polymerized, and esterified derivatives and salts, the aliphatic and

aromatic hydrocarbon resins, terpene resins and terpene-phenolic resins, and also C5, C9, and other hydrocarbon resins. Any desired combinations of these and further resins may be used in order to adjust the properties of the resultant adhesive in accordance with requirements. Generally speaking it is possible to employ any resins which are compatible (soluble) with the polyacrylate in question: in particular, reference may be made to all aliphatic, aromatic, and alkylaromatic hydrocarbon resins, hydrocarbon resins based on single monomers, hydrogenated hydrocarbon resins, functional hydrocarbon resins, and natural resins. Express reference may be made to the depiction of the state of the art in the "Handbook of Pressure Sensitive Adhesive Technology" by Donatas Satas (van Nostrand, 1989).

In a further advantageous onward development, the PSA is admixed with one or more plasticizers, such as low molecular mass polyacrylates, phthalates, water-soluble plasticizers, or plasticizing resins, for example.

The acrylate PSAs may further be blended with one or more additives such as aging inhibitors, light stabilizers, ozone protectants, fatty acids, resins, nucleators, expandants, compounding agents and/or accelerators. They may further be admixed with one or more fillers such as fibers, carbon black, zinc oxide, titanium dioxide, solid or hollow glass (micro)beads, microbeads made of other materials, silica, silicates, and chalk, and the addition of blocking-free isocyanates is possible as well.

Particularly for the method described it is of advantage if the polyacrylate is coated from the melt.

For this purpose the poly(meth)acrylates described in the foregoing are concentrated to give a hot-melt. This operation takes place preferably in a concentrating extruder. Here, the solvent is stripped off under reduced pressure, it being possible, for example, to use single-screw or twin-screw extruders, which advantageously distill off the solvent in different or identical vacuum stages, and which possess a feed preheater. Following the concentration process, the solvent content is preferably $\leq 2\%$ by weight, more preferably $\leq 0.5\%$ by weight.

In order to generate the structures, coating takes place through a die which is specially shaped as described above. Structuring can be undertaken in the die channel or else at the die exit, by emergence through a grid/screen/knifecoater, etc.

In order to retain the structuring of the PSA surface it is necessary for the PSA to be crosslinked immediately. Crosslinking is performed on a roll, which has to be provided with a contact medium, or on a support material. Where crosslinking takes place on a roll, in one preferred embodiment a chill roll is employed. The contact medium may in this case be applied either to the reverse of the PSA or to the chill roll described; it is, however, also possible for it to be applied contactlessly, by spray application, for example. One very preferred procedure for crosslinking can be found in application DE 100 14 563.

As a chill roll it is commonplace to use a grounded metal roll, which absorbs the electrons that strike it in the case of electron beam crosslinking, and the accompanying X-rays. It must be equipped with an effective cooling system in order to transport away the considerable quantities of heat. In order to prevent corrosion it is commonly coated with a protective coat. This coat is preferably selected such that it is wetted well by the contact medium. As a general rule, the surface is conductive. It can, however, also be more favorable to coat it with one or more coats of insulating or semiconducting material. Moreover, the cooling function ought to be very pronounced, in order to stabilize the PSA foam. In one preferred embodiment, therefore, cooling takes place to temperatures below 25°C, and in a very preferred embodiment to temperatures below 5°C.

The contact medium used can be a material which is capable of producing contact between the PSA and the roll surface, in particular a material which fills the cavities between structured PSA and roll surface.

Suitability for this purpose is exhibited by fluid materials, which may be present within a wide viscosity range. In addition, soft, "conformable" materials can be used as contact medium. On the one hand, with preference, soft and elastic materials can be used, such as plasticized rubber, plasticized PVC, other plasticized plastics and similar materials, for example. If they are firmly connected to the chill roll, they must exhibit sufficient radiation resistance and also sufficient thermal and electrical conductivity. In accordance with the invention it is particularly advantageous not to leave the contact medium permanently on the roll but instead to apply it to the roll before the irradiation operation and to remove it from the roll again after the irradiation operation. In a further advantageous embodiment the contact medium is in the form of a replaceable covering on the roll. Changeover of the contact medium can take place during the irradiation operation (continuous change-

over) or between the individual irradiation operations (discontinuous changeover). The continual replacement avoids the medium becoming so greatly impaired by the ongoing irradiation that it loses its function.

It has been found very advantageous in accordance with the invention to use, as the contact medium, a liquid, which if desired receives additives for additional functions. These include the increasing of wetting and of electrical conductivity, and the scavenging of free radicals and other reactive species generated by the absorbed radiation.

As a contact liquid it is possible with advantage to use water, which fulfills the necessary functions of the invention. In a further version, substances are added to the contact medium which are at least partly soluble therein. For water as contact medium, for example, appropriate additives include alkyl alcohols such as ethanol, propanol, butanol, and hexanol, without wishing by means of these examples to impose any restriction on the selection of the alcohols. Also very advantageous are alcohols, especially relatively long-chain alcohols, polyglycols, ketones, amines, carboxylates, sulfonates, and the like.

A lowering of the surface tension can also be achieved through the addition of small amounts of nonionic and/or anionic and/or cationic surfactants to the contact medium. The most simple way of achieving this is by using commercial washing compositions or soap solutions, preferably in a concentration of a few g/l in water, as the contact medium. Particularly suitable compounds are specific surfactants which can be used even at a low concentration. Examples thereof include sulfonium surfactants (e.g., β-di(hydroxy-alkyl)sulfonium salt), and also, for example, ethoxylated nonylphenylsulfonic acid ammonium salts. Here, reference may be made in particular to the state of the art under "surfactants" in Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, 2000 Electronic Release, Wiley-VCH, Weinheim 2000.

As contact media it is possible to use the aforementioned liquids, even without the addition of water, in each case alone or in combination with one another. In order to improve the properties of the contact medium (for example, to increase the shearing resistance, reduce the transfer of surfactants or the like to the liner surface, and thus improved cleaning possibilities for the end product), salts, gels, and similar viscosity-enhancing additives may also be added with advantage to the contact medium and/or to the adjuvants employed.

For the case of a liquid as the contact medium, one possible outstanding procedure is for a second roll, advantageously one with a wettable or absorbent surface, to run through a bath containing the contact medium, in doing so, to become wetted or impregnated with the contact medium, and to apply a film of this contact medium by contact with the chill roll.

In an embodiment which is very preferred for the invention the structured PSA is crosslinked on the contact medium. This may take place by means of electron beams and/or by means of UV irradiation.

Typical irradiation equipment which is employed in the case of the inventive design of the method with electron-beam crosslinking includes linear cathode systems, scanner systems and segmented cathode systems, where electron-beam accelerators are concerned. An extensive description of the state of the art and of the most important process parameters is found in Skelhorne, "Electron Beam Processing", in Vol. 1 of "Chemistry & Technology of UV and EB Formulation for Coatings, Inks and Paints", publ. SITA Technology, London 1991.

The acceleration voltages are situated in the range between 40 kV and 500 kV, preferably 80 kV and 300 kV. The radiation doses employed range between 5 to 150 kGy, in particular 20 to 100 kGy.

As a result of the method using a chill roll, the radiation doses needed for crosslinking can be chosen to be significantly higher as compared with conventional crosslinking methods.

The inventive method further provides for UV crosslinking by means of brief ultraviolet irradiation in a wavelength range from 200 to 450 nm, in particular using high-pressure or medium-pressure mercury lamps with an output of 80 to 240 W/cm. For UV crosslinking it is also possible, however, to use monochromatic radiation in the form of lasers. In order to prevent instances of overheating it may be appropriate to carry out partial shading of the UV beam path. Furthermore, special reflector systems can be used, which function as cold light emitters in order thus to prevent overheating.

Following crosslinking, the structured PSAs are applied to a backing material or laminated with a further PSA.

The onward guiding of the backing materials is advantageously performed under a certain applied pressure. By this means it is ensured that, on the one hand, no air bubbles are included and, on the other hand, the amount of contact liquid is limited to the necessary extent. The applied pressure can be achieved by setting a suitable web tension or by pressure contact with a roller. In this case the surface of the pressure roller must exhibit a certain release effect, so that the PSA layer on the surface of the backing does not stick to it. Further possibilities would be the application of pressure by air jet or air cushion, or by electrostatic forces.

In addition to the described methods of coating onto a roll to be provided with the contact medium, and of crosslinking on this roll with subsequent transfer to the backing material, the structured PSA can also be coated directly onto a backing material and crosslinked thereon.

Backing materials used for the structured PSA, in its utility for PSA tapes, for example, are the materials which are customary and familiar to the skilled worker, such as films (polyester, PET, PE, PP, BOPP, PVC), nonwovens, foams, woven fabrics and woven films, and also release paper (glassine, HDPE, LDPE). This enumeration is not exhaustive.

For the inventive method it is very advantageous if the time between structuring in or after the die, and crosslinking, is kept particularly short. In one preferred embodiment crosslinking takes place in less than 5 seconds after structuring, and hence in a continuous method.

For the inventive method it may further be of advantage if the hot, structured acrylate PSA emerging through the outlet is cooled directly. This is best done by cooling with air or by means of the described chill roll with contact medium, or by means of a chill roll which in one preferred embodiment likewise contains a contact medium, and cools the backing material of the PSA assembly.

By virtue of the inventive method it is likewise possible to produce oriented structured PSA. For this purpose, in one preferred embodiment, PSAs having a high average molecular weight are coated through a die. By means of the die geometry and the drawing to a relatively low layer thickness, it is possible to achieve an orientation of the

structured PSA with particular preference in the machine direction, and for this orientation to be frozen in by the direct cooling and immediate crosslinking with electron beams or UV light. Structured PSAs of this kind have an intensified anisotropic behavior, which also relates, for example, to the tensile/elongation characteristics of the PSA.

Claimed below is the use of the structured PSA produced by the inventive method as a pressure-sensitive adhesive tape.

Of particular advantage is the use of the PSAs or PSA foams produced as described for an adhesive tape, it being possible for the PSA to be applied to one or both sides of a backing.

Structured PSA tapes may have numerous advantages. As a result of the structuring, the bond area is reduced, and PSA tapes of this kind can therefore be repositioned very well. Furthermore, these PSA tapes also possess a relatively low peel release, so that a further application is that of redetachable bonds (temporary bonds with PSA tapes).

Furthermore, the anisotropic properties can be utilized, for example, in connection with the removal of PSA tapes from a substrate, since the PSA tape possesses a different bond strength in the longitudinal direction to that in the transverse direction. For the detachment operation it may therefore be of advantage to remove the PSA tape in the direction of the lower bond strength. The user therefore requires a lower force for this operation. If shearing forces or stress on the PSA tape occur in one direction, it is then possible, in turn, to choose the direction such that the PSA tape possesses a higher bond strength in the direction of stress.

The invention is illustrated below with reference to examples.

<u>Examples</u>

<u>Preparation of acrylate PSA 1</u>

A 200 L reactor conventional for free-radical polymerizations was charged with 2400 g of acrylic acid, 3200 g of N-tert-butylacrylamide, 4000 g of methyl acrylate, 30.4 kg of 2-ethylhexyl acrylate, and 30 kg of acetone/isopropanol (97:3). After nitrogen gas had been passed through the reactor for 45 minutes with stirring, the reactor was heated to 58°C and 20 g of 2,2'-azoisobutyronitrile (AIBN) were added. Subsequently the external

heating bath was heated to 75°C and the reaction was carried out constantly at this external temperature. After a reaction time of 1 h a further 20 g of AIBN were added. The reaction was terminated after a time of 48 h, and cooling was carried out to room temperature. Thereafter the PSA was freed from the solvent with heating and with application of a vacuum. The residual solvent fraction was < 0.5%.

Preparation of acrylate PSA 2

A 200 L reactor conventional for free-radical polymerizations was charged with 3600 g of acrylic acid, 36.4 kg of 2-ethylhexyl acrylate, and 30 kg of acetone/isopropanol (97:3). After nitrogen gas had been passed through the reactor for 45 minutes with stirring, the reactor was heated to 58°C and 20 g of 2,2'-azoisobutyronitrile (AIBN) were added. Subsequently the external heating bath was heated to 75°C and the reaction was carried out constantly at this external temperature. After a reaction time of 1 h a further 20 g of AIBN were added. The reaction was terminated after a time of 48 h, and cooling was carried out to room temperature. Thereafter the PSA was freed from the solvent with heating and with application of a vacuum. The residual solvent fraction was < 0.5%.

Coating

The acrylate hotmelts were conveyed by means of a single-screw extruder (L/D: 27). Coating took place through a die with a 300 μm slot constructed in accordance with fig. 1 (b). Accordingly, structuring of the PSA was performed at the top exit lip. Over a width of 30 cm a structure with a depth of 100 μm was incised. From this width the die contained 60 jags, so that the base area of each jag was 0.5 cm.

The hotmelt PSA structured in this way was laminated directly onto a 23 μm, corona-pretreated PET film. The average coatweight was 50 g/m^2. In the course of the coating operation, the PET film is guided over a chill roll. The temperature of the chill roll was approximately 4°C. Subsequently the composite was crosslinked directly with electron beams in an in-line process.

Electron beam irradiation

Electron beam irradiation was carried out using an instrument from Electron Crosslinking AB, Halmstad, Sweden. The PSA for irradiation was guided via a chill roll beneath the Lenard window of the accelerator. Atmospheric oxygen in the zone of irradiation was displaced by flushing with pure nitrogen. The belt speed was 10 m/min. Crosslinking took place with 50 kGy at an acceleration voltage of 180 kV.

Adhesive bonding

The peel strength (bond strength) was tested in accordance with PSTC-1. A strip of this specimen 2 cm wide is adhered to a steel plate by being rolled over back and forth three times using a 2 kg roller. The plate is clamped in and the self-adhesive strip is pulled via its free end in a tensile testing machine at a speed of 300 mm/min under a peel angle of 180°. To investigate the anisotropic properties, the PSA strips were cut in one instance in the longitudinal and in one instance in the transverse direction. The results are summarized in table 1.

Table 1

	BS-long [N/cm]	BS-cross [N/cm]
Example 1	2.1	3.2
Example 2	1.9	2.8

BS = bond strength in newtons/cm

long = longitudinal or machine direction/coating direction

cross = transverse to the machine direction/coating direction